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Etherification Optimization for Preparing Partially Hydrolized Hydroxypropylated Guar Gum and Its Properties

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ABSTRACT: The partially hydrolized hydroxypropylated guar gum (PHHGG) was prepared using GG as the raw material, hydrochloric acid as the hydrolysis agent, epoxy propane as the etherifying agent, ethanol as the solvent to obtain better property combination. The effect of the reaction temperature, reaction time, and amounts of sodium hydroxide, ethanol, and epoxy propane on the substitution degree of the partially hydrolized hydroxypropylated GG was investigated. These process parameters were optimized by the orthogonal test. Using polarized light microscopy, infrared spectrometer, differential scanning calorimetry, and thermogravimetric analyzer, the appearance, structure, and thermal property of the partially hydrolized hydroxypropylated GG (PHHGG) were observed and measured. The results indicated that the best process conditions for preparing the PHHGG were: reaction temperature = 60°C, reaction time = 12 h, amount of sodium hydroxide = 1.2%, amount of ethanol = 60%. The acid resistance and alkali resistance of GG were obviously improved by the acidolysis and hydroxypropylation. The particle appearance of GG was a thin strip after it was hydrolized by acid and hydroxypropylated by epoxy propane. The acidolysis increased the melting onset temperature, peak temperature, and end temperature of GG but the hydroxypropylation decreased them. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40489.

KEYWORDS: guar gum; acidolysis; hydroxypropylation; property

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INTRODUCTION

Guar gum (GG) is a linear galactomannan, belonging to the non-ion–type polymer.[1] Guar gum quickly became the environmentally friendly material with excellent performance because of its unique molecular structure and natural characteristics. So it is widely used in water treatment, paper making, food, medicine, and other fields.[2,3] However, the practical application of GG is that it is difficult to achieve the satisfactory results owing to the shortcomings such as the slow dissolution rate, high water insoluble content, difficult controlling viscosity, and susceptible to microbial contamination. As a result, ways to improve its performance were sought. At present, GG is mainly modified by the etherification, esterification, oxidation, crosslinking, and enzymatic hydrolysis to improve its performance.[4–8] Guar gum and its derivatives are water-soluble hydrophilic polymers whose solutions are highly viscous in nature. The hydrophobic nature of the polymer increases through the hydroxypropylation of acryloyl chloride, which results in an increased compatibility.[9] Partially hydrolyzed GG (PHGG) has been shown to suppress postprandial serum lipid levels in healthy and moderate hypertriglyceridemia volunteers after a high-fat high-cholesterol meal. The bioaccessibility showed a decrease depending on the PHGG dose.[10] Partially hydrolized GG has low viscosity, high gel strength, and good water solubility.[11,12] Hydroxypropylated GG (HPGG) has high transparency and good salt, acid, and alkali resistances.[13–16] After GG is modified by acid hydrolysis and hydroxypropylation, however, its product will, therefore, have the combined characteristics of the PHGG and HPGG, which further improved its application and expanded its application scope. The purpose of this work is to optimize the parameters for preparing PHHGG by the orthogonal test. At the same time, its properties were measured so as to explore the use of natural, eco-friendly, renewable resources as additives in the industry.

MATERIALS AND METHODS

Materials

Guar gum was purchased from Binzhou Zhongbo Chemical Co. Sodium hydroxide was purchased from Tianjin Bodi Chemical Co. Ethanol was purchased from Tianjin Fuyu Fine Chemical Co. Epoxy propane was purchased from Sinopharm Chemical Reagent Co. Ninhydrin was purchased from Tianjin Kemiou Chemical Reagent Co. Sulfuric and hydrochloric acids were purchased from Shenyang Paier Fine Chemical Factory. All the above reagents were of analytical grade.

Preparation of PHHGG

Partially Hydrolized GG. Guar gum was weighed and 95% aqueous ethanol solution was added to produce GG slurry with a concentration of 35% (w/w) by mass basis. The slurry was poured into a 250-mL three-necked flask and stirred. A certain quantity of hydrochloric acid with a concentration of 36% (w/w) (the mass ratio of hydrogen chloride to dry GG 1 : 100) was added after the resultant slurry was heated in the water bath at 40°C. Guar gum was hydrolyzed by acid for 4 h at a constant temperature. After the completion of hydrolysis, the slurry was neutralized by sodium hydroxide-aqueous ethanol solution with a concentration of 16.7% (the mass ratio of sodium hydroxide to ethanol 2 : 5) to a pH of 6.5–7.0. The vacuum filtration of the slurry was completed. The obtained filtered cake was washed four times using 95% aqueous ethanol solution. The resultant cake was dried at 100°C for about 4 h in a 1010-2 electrothermal constant-temperature dry box (Jintan City Dadi Automation Instrument Factory, China) so the moisture content could be less than 12%. The dried cake was grounded and screened. Finally, PHGG was obtained.

Partially Hydrolized Hydroxypropylated GG. The PHGG powder (20 g, dry basis, fluidity 39.8 mL) was weighed and then 95% aqueous ethanol solution was added to produce the PHGG slurry with a mass concentration of 30%. The slurry was put into the 250-mL three-necked flask. Sodium hydroxide was added, stirred, and heated in a water bath at a required temperature. The propylene oxide was quickly added into the suspension and sealed. The reaction was maintained at a constant temperature for 8∼16 h. After the reaction was completed, the slurry was neutralized with dilute hydrochloric acid with a mass concentration of 10% to a pH of 6.5–7.0. The vacuum filtration of the slurry was completed. The obtained filtered cake was washed four times using 95% aqueous ethanol solution. The resultant cake was dried at 100°C for about 4 h in a 1010-2 electrothermal constant-temperature dry box (Jintan City Dadi Automation Instrument Factory) so the moisture content could be less than 12%. The dried cake was grounded and screened. Finally, PHHGG was obtained. The preparation of HPGG is similar to the above method.

Determination of Degree of Substitution

About 0.08 g of the dry specimen was weighed accurately and then put into the volumetric flask. Sulfuric acid (25 mL; 0.5 mol/L) was added to cleave the ether bond producing propylene glycol. The mixture was digested in a boiling water bath until a clear solution was obtained. The resulting clear solution was cooled and diluted to 100 mL with distilled water. One milliliter of the solution was pipetted into a 25-mL graduated test tube and immersed in the cold water. About 8 mL of the concentrated sulfuric acid was added dropwise into the tube. After thorough shaking, the tube was placed in the boiling water bath for 3 min. The tube was immediately cooled to 5°C in an ice bath. About 0.5 mL of ninhydrin solution was added into the tube. After the solution was shaken well, the tube was placed in a water bath and kept at constant temperature for 100 min at 25°C. The solution was then made up to 25 mL with concentrated sulfuric acid and thoroughly mixed. It was transferred to a 1-cm cell of a WFJ 7200 type spectrophotometer (Shanghai Unico Instrument Co., Ltd., China), and after 5 min, the absorbance was measured at 595 nm.

The GG blank was used as reference. A calibration curve was prepared with an aliquot (1 mL) of the standard aqueous solutions, containing 10, 20, 30, 40, and 50 μg of propylene glycol per milliliter. The calibration curve was showed in Figure 1. The propylene glycol concentration in the specimen was calculated from the standard curve and was converted to the equivalent hydroxypropyl groups from each molar solution using the following equations[17–19]:

$$\mathrm{MS} = \frac{2.79H}{100-H}$$

$$H = F\left(\frac{M_{\mathrm{sample}}}{W_{\mathrm{sample}}} - \frac{M_{\mathrm{blank}}}{W_{\mathrm{blank}}}\right) \times 0.7763 \times 100$$

where, MS, molar substitution degree; H, hydroxypropyl content, %; F, dilution multiple of sample and F was equal to 100; M_{sample}, propylene glycol content of sample obtained from the standard curve, g; W_{sample}, sample quality, g; M_{blank}, propylene glycol content of blank sample obtained from the standard curve, g; W_{blank}, sample mass of GG, g.

Acid and Alkali Resistances

The sample paste with a mass concentration of 1% (w/w) by the dry GG derivative was produced using distilled water. The sample paste was heated in a boiling bath under constant agitation till it became a complete paste. Then the paste was cooled in cold water to required temperature. The pH value of the paste was adjusted to 10 or 3, and the paste was stirred using a glass bar for 5 min. The viscosity of the paste was then measured by a NDJ-1 rotary viscometer (Shanghai Tianping Instrument Factory, China) at a constant temperature (25°C). The viscosity of the sample changed slightly, which meant strong acid and alkali resistances. The measurement method of the acid and alkali resistances of GG was similar to that of the GG derivative.[20,21]

Infrared Spectroscopy

A IR Prestige-21 infrared spectrometer (Shimadzu Corporation, Japan) was used to record the Infrared (IR) spectra within the range of 4000∼400 cm^{-1}. The IR spectra were recorded in the solid state using a KBr pellet method. The dry sample was blended with KBr in a ratio starch/KBr 1 : 100. Then the blend was pressed to obtain a pellet.

Particle Morphology

The particle morphology was observed by a XPL-2 transflective polarizing microscope (Nanjing Jiangnan Yongxin Optics Company Limited, China). About 5 mg of the sample was placed on a clean slide. A few drops of ethanol were added to the slide. A cover glass was used to cover the sample particles and then moved back and forth until these particles were uniformly dispersed on the slide. The cover glass was removed. The lighting power of the polarizing microscope was opened. Appropriate magnification was selected, and then the light source was adjusted and focused. The slide with the sample particles was put and moved under the object lens of the polarizing microscope. The appropriate viewing area was

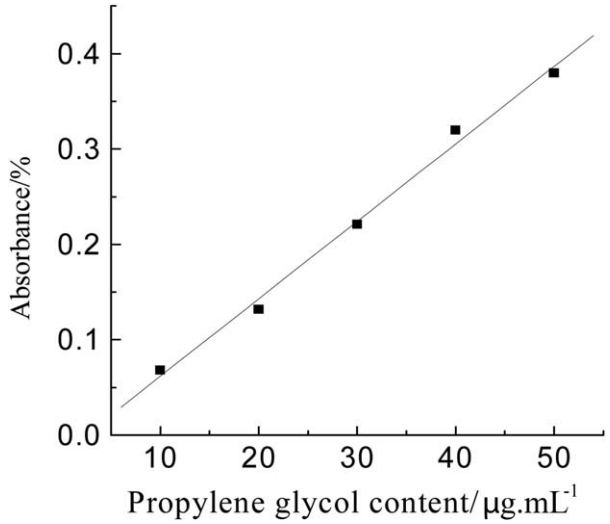

Figure 1. Relationship between propylene glycol content and absorbance.

selected to observe the size and the shape of the sample particles.[22]

Thermal Analysis

The thermal analysis of GG or its derivative was carried out with a TGA Q50 V20.10 Build 36 thermogravimetric analyzer (TGA) and a DSC Q20 V24.4 Build 116 differential scanning calorimeter (DSC; TA Instruments) in a nitrogen atmosphere. To properly characterize the thermal properties of GG, PHGG, and PHHGG, the mixture needed to be analyzed in a sealed pan in order to prevent the loss of water from the formulation during heating.

Analysis conditions of DSC: sample mass = 3.0∼5.5 mg, heating rate = 10°C/min, temperature range = 10∼200°C.[23]

Analysis conditions of TGA: sample mass = 15.0∼16.0 mg, heating rate = 10°C/min, temperature range = 10∼800°C.[24]

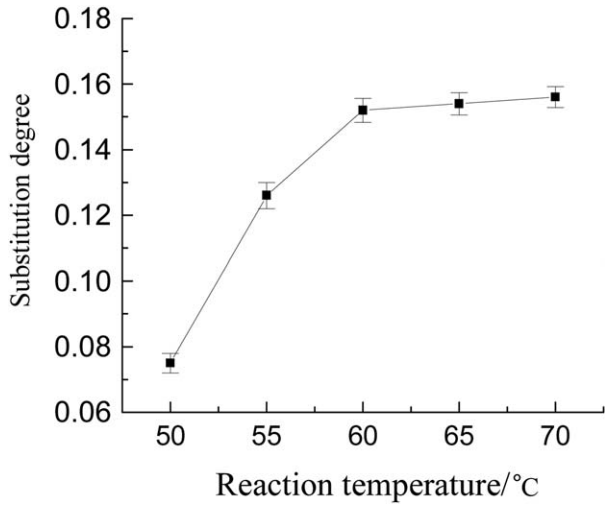

Figure 2. Effect of reaction temperature on the substitution degree of PHHGG.

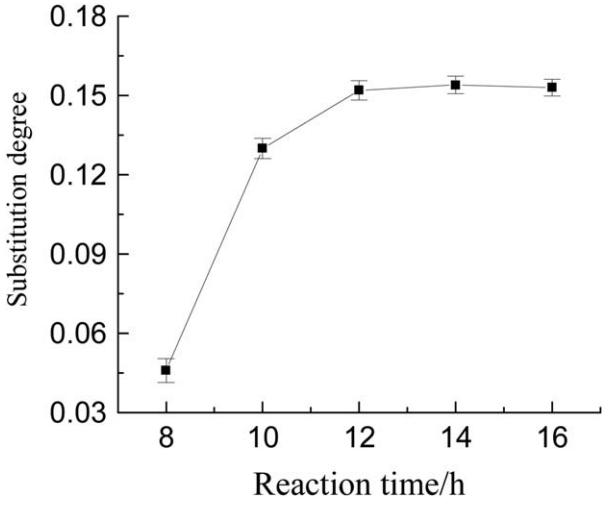

Figure 3. Effect of reaction time on the substitution degree of PHHGG.

RESULTS AND DISCUSSION

Effect of Reaction Temperature on Substitution Degree

The effect of reaction temperature on the substitution degree of PHHGG is shown in Figure 2. Reaction conditions: PHGG powder 21.56 g (fluidity 39.8 mL, moisture content 7.23%), mass concentration of slurry 30%, reaction time 12 h, amount of ethanol 60% (the percentage of the mass ratio of ethanol to slurry), amount of sodium hydroxide 1.2% (the percentage of the mass ratio of sodium hydroxide to dry GG), amount of epoxy propane 15% (the percentage of the mass ratio of epoxy propane to dry GG).

The reaction temperature was varied from 50 to 70°C to examine the temperature effects. The substitution degree of PHHGG increased with the increase of the reaction temperature when the reaction temperature < 60°C. The substitution degree of PHHGG did not increased basically with the increase of the reaction temperature when the reaction temperature > 60°C. The reason might be explained as: as the reaction temperature increased, the molecular thermal motion was accelerated, which resulted in favor of the etherification reaction. However, the elevated temperature could produce the large expansion of the GG grains and increase the evaporation rate of ethanol and propylene oxide. As a result, the substitution degree of PHHGG was basically unchanged from 60 to 70°C. So the suitable reaction temperature was considered to be 60°C.

Effect of Reaction Time on Substitution Degree

The effect of reaction time on the substitution degree of PHHGG is shown in Figure 3. Reaction conditions: PHGG powder 21.56 g (fluidity 39.8 mL, moisture content 7.23%), mass concentration of slurry 30%, reaction temperature 60°C, amount of ethanol 60%, amount of sodium hydroxide 1.2%, amount of epoxy propane 15%.

From Figure 3 it can be inferred that the substitution degree of PHHGG increased with increasing reaction time, when the reaction time was below 12 h. The substitution degree of PHHGG was basically unchanged when the reaction time was above 12

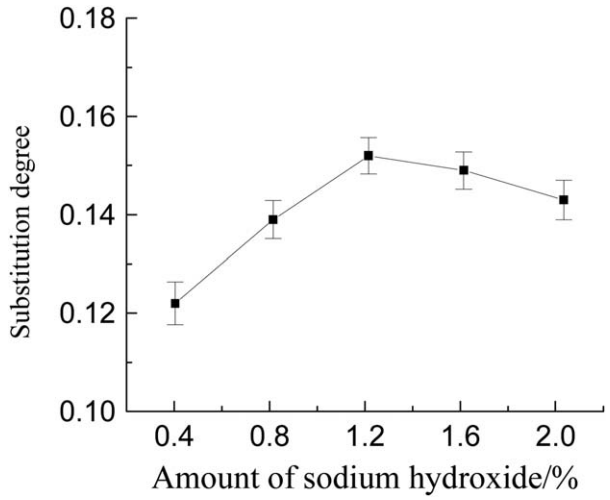

Figure 4. Effect of amount of sodium hydroxide on the substitution degree of PHHGG.

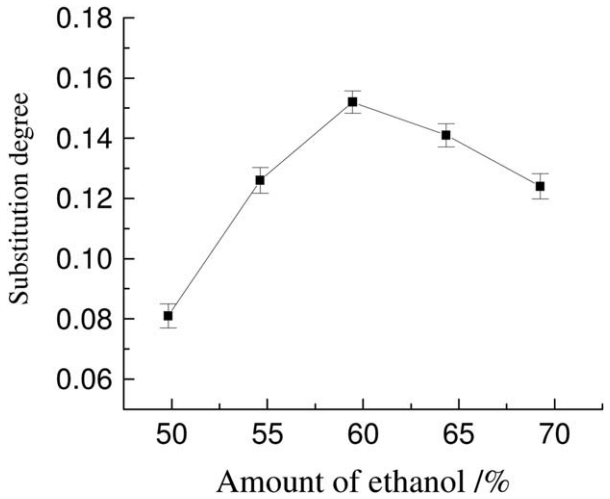

Figure 6. Effect of amount of ethanol on the substitution degree of PHHGG.

h. The cause for this could be explained as follows. As the reaction time increased, the increase of the effective contact between the molecules of PHGG and the molecules of epoxy propane promoted the etherification reaction. Conversely, as the reaction was conducted, epoxy propane in the system also decreased gradually. Especially, when epoxy propane was below a certain concentration, the substitution degree of PHHGG did not vary with increasing reaction time. So the suitable reaction time was considered to be 12 h.

Effect of Amount of Sodium Hydroxide on Substitution Degree

The effect of the amount of sodium hydroxide on substitution degree of PHHGG is shown in Figure 4. Reaction conditions: PHGG powder 21.56 g (fluidity 39.8 mL, moisture content 7.23%), mass concentration of slurry 30%, reaction temperature 60°C, reaction time 12 h, amount of ethanol 60%, amount of epoxy propane 15%.

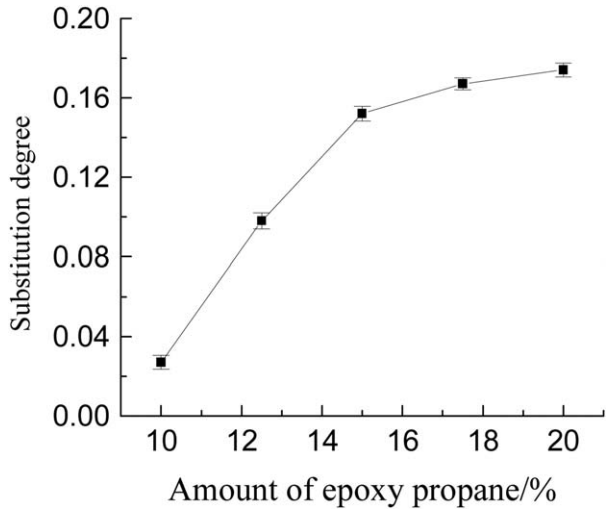

Figure 5. Effect of amount of epoxy propane on the substitution degree of PHHGG.

The amount of sodium hydroxide was varied from 0.4% to 2.0% to examine its effects. From Figure 4 it can be inferred that the substitution degree of PHHGG increased with increase in the amount of sodium hydroxide when the amount of sodium hydroxide was below 1.2%. However, when the amount of sodium hydroxide was above 1.2%, the substitution degree of PHHGG decreased with the increase in the amount of sodium hydroxide. Sodium hydroxide not only acted as a catalyst during the etherification reaction but also promoted the expansion of the GG particles, which was in favor of epoxy propane molecules entering into the internal grains of GG for the polymers. When the amount of sodium hydroxide was below 1.2%, the catalysis of sodium hydroxide predominated, and the etherification efficiency was high. It resulted in the increase of the substitution degree with increasing amount of sodium hydroxide. However, when the amount of sodium hydroxide was above 1.2%, sodium hydroxide could cause the excessive expansion of the GG particles, which reduced the effective contact between the —OH groups of the GG molecules and the epoxy propane molecules. It was not conducive to the etherification reaction. Furthermore, the solubility of sodium hydroxide in the alcohol solution was the rate-determining variable in the reaction. Therefore, the suitable amount of sodium hydroxide was considered to be 1.2%.

Effect of Amount of Epoxy Propane on Substitution Degree

The effect of the amount of epoxy propane on the substitution degree of PHHGG was showed in Figure 5. Reaction conditions: PHGG powder 21.56 g (fluidity 39.8 mL, moisture content 7.23%), mass concentration of slurry 30%, reaction temperature 60°C, reaction time 12 h, amount of ethanol 60%, amount of sodium hydroxide 1.2%.

The amount of epoxy propane was varied from 10% to 20% to examine the effects of epoxy propane amount. From Figure 5 it can be inferred that the substitution degree of PHHGG increased rapidly with the increase of the amount of epoxy propane when the amount of epoxy propane was less than 15%. When the amount of propylene oxide was greater than 15%,

Table I. Factor and Level of Orthogonal Test

Factor levels	Reaction temperature, *A* (°C)	Reaction time, *B* (h)	Amount of sodium hydroxide, *C* (%)	Amount of ethanol, *D* (%)
1	55	10	0.8	55
2	60	12	1.2	60
3	65	14	1.6	65

however, the increase of the substitution degree became slow. The reasons for this phenomenon could be explained as: on the surface of GG particles, the number of the hydroxyl group was fixed. Conversely, the side reaction increased with increasing amount of epoxy propane, and hydroxypropyl radicals also increased the space resistance effect. Therefore, the suitable amount of propylene oxide was considered to be 15%.

Effect of Amount of Ethanol on Substitution Degree

The effect of the amount of ethanol on the substitution degree of PHHGG is shown in Figure 6. Reaction conditions: PHGG powder 21.56 g (fluidity 39.8 mL, moisture content 7.23%), mass concentration of slurry 30%, reaction temperature 60°C, reaction time 12 h, amount of epoxy propane 15%, amount of sodium hydroxide 1.2%.

From Figure 6 it can be inferred that when the amount of ethanol was less than 60%, the substitution degree of PHHGG increased with increasing the amount of ethanol. However, when the amount of ethanol was greater than 60%, the substitution degree decreased with increasing the amount of ethanol. Ethanol as a solvent acted as restricting the swelling of the particles of GG. When the amount of ethanol was small, the more sodium hydroxide was capable to be dissolved in water due to the constant concentration of the slurry, which was conducive to the moderate swelling of the GG particles and the etherification reaction. However, when the amount of ethanol was large, less sodium hydroxide was dissolved in water so that GG particles were not able to be fully swelled. It reduced the efficiency of the etherification reaction. Therefore, the suitable amount of ethanol was considered to be 60%.

Orthogonal Test for Optimal Etherification Parameters of PHHGG

To optimize the hydroxypropylation of PHGG, four responses with desirable criteria were chosen to be limiting factor. The substitution degree was selected with the intention to achieve the highest possible value. Design and result of the orthogonal test are shown in Tables I and II. The amount of epoxy propane was held at 15%.

Table II. Design and Result of Orthogonal Test

Test number	*A*	*B*	*C*	*D*	Substitution degree
1	1	1	1	1	0.072
2	1	2	2	2	0.142
3	1	3	3	3	0.115
4	2	1	2	3	0.119
5	2	2	3	1	0.128
6	2	3	1	2	0.132
7	3	1	3	2	0.125
8	3	2	1	3	0.108
9	3	3	2	1	0.121
k_1	0.110[a]	0.105	0.104	0.107	
k_2	0.126	0.126	0.127	0.133	
k_3	0.118	0.123	0.123	0.114	
R	0.016[b]	0.021	0.023	0.026	

[a] K^a_i = Σ reaction temperature at A_i/3.
[b] R^a_i = max $\{k^a_i\}$ − min $\{k^a_j\}$.

The orthogonal test table was designed to detect the most suitable etherification conditions of four factors (reaction temperature, reaction time, amount of sodium hydroxide, amount of ethanol). According to the value of *R* in Table II, the amount of ethanol (factor *D*) exerted the most significant effect on the substitution degree, and the order of the importance that influenced the substitution degree was found to be the amount of ethanol (*D*) > amount of sodium hydroxide (*C*) > reaction time (*B*) > reaction temperature (*A*). Under the optimum conditions, the substitution degree of PHHGG reached to 0.155. The optimal combination parameters for preparing PHHGG were $A_2B_2C_2D_2$, namely, reaction temperature 60°C, reaction time 12 h, amount of sodium hydroxide 1.2%, amount of alcohol 60%.

Acid and Alkali Resistances

The acid and alkali resistances of GG, PHGG, HPGG, and PHHGG are shown in Table III.

From Table III, it can be inferred that after GG was partially hydrolized by acid or hydroxypropylated, its viscosity decreased, but the acid and alkaline resistances increased. It proved that the acidolysis and hydroxypropylation could obviously improve its acid and alkali resistances. The viscosity of PHGG increased in the acidic or alkaline environment. The viscosity of HPGG and PHHGG reduced in the acidic environment, whereas their viscosity increased in the alkaline environment.

Table III. Acid and Alkali Resistances

Sample	Viscosity (mPa s) (pH = 6.8)	Viscosity (mPa s) (pH = 3)	Viscosity (mPa.s) (pH = 10)
GG	9000 ± 280	10,450 ± 310	10,660 ± 310
PHGG (Fluidity = 39.8 mL)	90 ± 3.1	94 ± 3.3	99 ± 3.5
HPGG (MS = 0.214)	1596 ± 54	1472 ± 50	1776 ± 60
PHHGG (Fluidity = 39.8mL, MS = 0.152)	84 ± 2.9	81 ± 2.8	87 ± 3.0

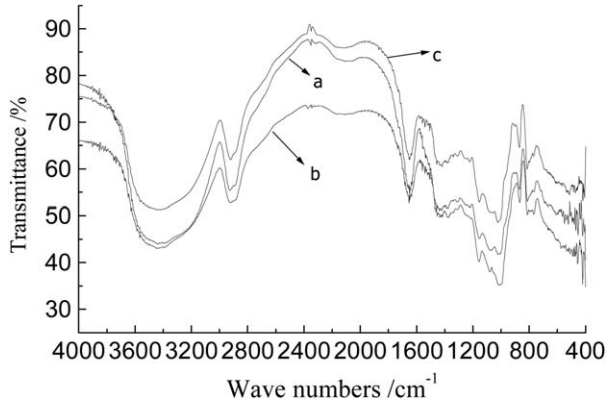

Figure 7. FT-IR spectra of GG, PHGG, and PHHGG.

Infrared Spectroscopy

FT-IR spectra of GG, PHGG (Fluidity = 39.8 mL), and PHHGG (Fluidity = 39.8 mL, MS = 0.152) are shown in Figure 7.

From Figure 7, it can be inferred that there was basically no difference in shape among FT-IR spectra of GG, PHGG, and PHHGG, except the peak intensity. The absorption peak at wave number 3421 cm^{-1} was attributed to the stretching vibration of the O—H bond. The absorption peak at wave number 2930 cm^{-1} belonged to the stretching vibration of the C—H bond, and at wave number 1160 cm^{-1} belonged to the stretching vibration of the C—O—C bond. The absorption peak at wave number 860 cm^{-1} was attributed to the C—C backbone vibration.

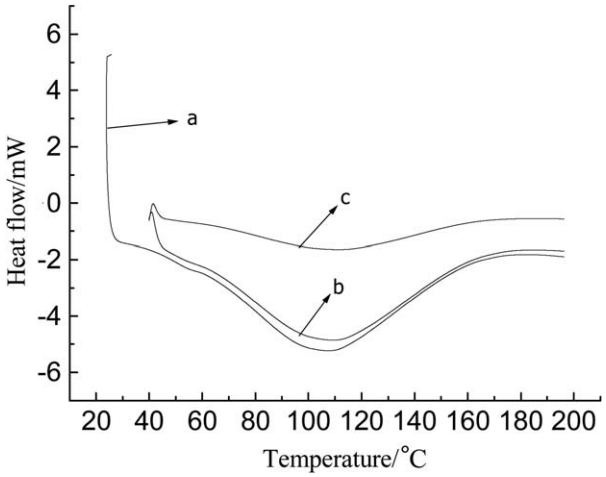

Figure 9. DSC curves of GG, PHGG, and PHHGG.

The Particle Morphology

The polarizing microscope photos of GG, PHGG (Fluidity = 39.8 mL), and PHHGG (Fluidity = 39.8 mL, MS = 0.152) were showed in Figure 8.

From Figure 8, it can be inferred that there was no Maltese cross on the surface of the particles of GG, which was very different from the particles of starches. The shape of the GG particles was irregular and thick. After GG was partially hydrolized or partially hydrolized and hydroxypropylated, its appearance was changed into a thin strip and its size was also reduced. The

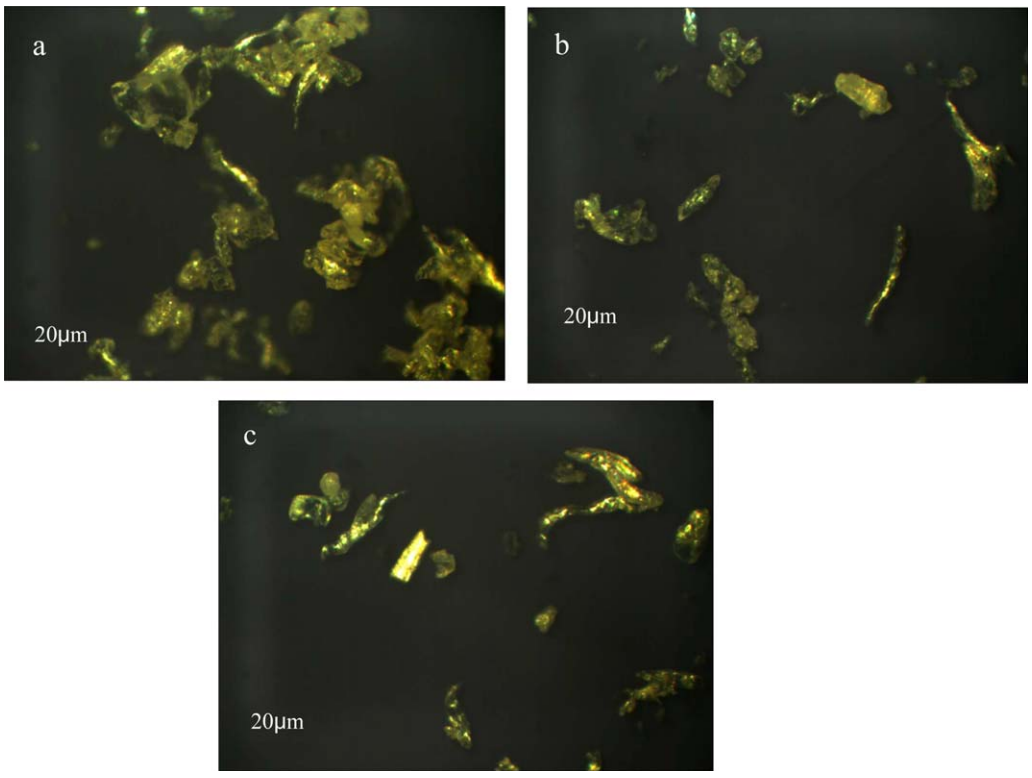

Figure 8. Polarizing microscope photos of GG, PHGG, and PHHGG (×125). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

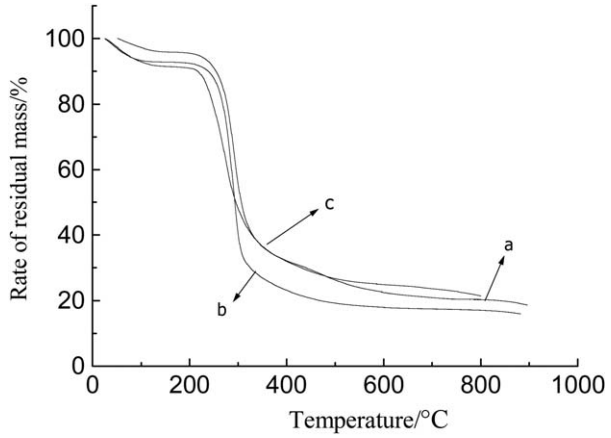

Figure 10. TGA curves of GG, PHGG, and PHHGG.

Table IV. Onset Temperature, Peak Temperature, End Temperature, and Melting Enthalpy

Sample	Onset temperature (°C)	Peak temperature (°C)	End temperature (°C)	Melting enthalpy (J g^{-1})
GG	27.89	106.77	163.96	227.6
PHGG	44.58	110.73	168.78	216.2
PHHGG	43.43	108.26	162.27	119.7

structure of the GG granules was apparently destroyed by this acid hydrolysis.

DSC and TGA Analyses

The DSC and TGA curve of GG, PHGG (Fluidity = 39.8 mL), and PHHGG (Fluidity = 39.8 mL, MS = 0.152) are shown in Figures 9 and 10.

According to Figures 9 and 10, after GG was modified by acidolysis and hydroxypropylation, its onset temperature, peak temperature, end temperature, melting enthalpy of the absorption peak, thermal stability all were changed. The specific parameters calculated by the aforementioned figures were shown in Tables IV and V.

From Tables IV and V, the onset temperature, peak temperature of PHGG and PHHGG were more than those of GG, but their melting enthalpy less than that of GG. The lower enthalpy value of PHGG and PHHGG was due to partial disorganization of GG components, and the disruption of GG granules during this chemical modification was responsible of this behavior. The acidolysis was able to increase the onset temperature, peak temperature and end temperature of GG. These higher temperatures of PHGG could be attributed to its larger proportion of short chains. However, the onset temperature, peak temperature, end temperature, and melting enthalpy of GG reduced owing to hydroxypropylation, compared with those of PHGG. The acidolysis decreased the onset decomposition temperature and end decomposition temperature of GG, but the hydroxypropylation increased its onset decomposition temperature and end decomposition temperature. The thermal stability of GG was lowered by the acidolysis or hydroxypropylation.

Table V. Onset Decomposition Temperature, End Decomposition Temperature, Mass Loss Rate

Sample	Onset decomposition temperature (°C)	End decomposition temperature (°C)	Rate of weight loss (%)
GG	227.60	440.35	60.71
PHGG	220.11	427.99	69.77
PHHGG	260.20	453.80	69.84

CONCLUSIONS

The best technologic conditions for preparing PHHGG are: reaction temperature = 60°C, reaction time = 12 h, amount of sodium hydroxide = 1.2%, amount of ethanol = 60%. The order of importance that influenced the substitution degree was found to be the amount of ethanol > amount of sodium hydroxide > reaction time > reaction temperature.

After GG was partially hydrolized by acid or hydroxypropylated, its viscosity decreased, but the acid and alkaline resistance increased. The viscosity of HPGG, PHHGG in the acidic environment was different from that in the alkaline environment. The appearance of PHGG and PHHGG particles was a thin strip. The acidolysis was able to increase the onset temperature, peak temperature, and end temperature of GG but the hydroxypropylation was opposite. The acidolysis or hydroxypropylation lowered the thermal stability of GG.

REFERENCES

1. Dodi, G.; Hritcu, D.; Popa, M. I. *Cellul. Chem. Technol.* **2011**, *45*, 171.
2. Sharma, R. *Asian J. Exp. Sci.* **2005**, *19*, 277.
3. Bhaskar, S. G.; Jubilant, E. A. *Eur. Food Res. Technol.* **2005**, *221*, 746.
4. Yannan. C.; Xiaoyan, W.; Xia, M.; Jia, L.; Bo, J. *Carbohydr. Polym.* **2010**, *82*, 829.
5. Fujioka, R.; Tanaka, Y.; Yoshimura, T. *J. Appl. Polym. Sci.* **2009**, *114*, 612.
6. Barbucci, R.; Pasqui, D.; Favaloro, R. *Carbohydr. Res.* **2008**, *343*, 3058.
7. Gong, H.; Liu, M.; Zhang, B.; Cui, D.; Gao, C.; Ni, B.; Chen, J. *Int. J. Biol. Macromol.* **2011**, *49*, 1083.
8. Mudgil, D.; Barak, S.; Khatkar, B. S. *Int. J. Biol. Macromol.* **2012**, *50*, 1035.
9. D'Melo, D. J.; Shenoy, M. A. *Polym. Bull.* **2008**, *61*, 235.
10. Minekus, M.; Jelier, M.; Xiao, J. Z.; Kondo, S.; Iwatsuki, K.; Kokubo, S.; Bos, M.; Dunnewind, B.; Havenaar, R. *Biosci. Biotechnol. Biochem.* **2005**, *69*, 932.
11. Sarkar, S.; Singhal, R. S. *Carbohydr. Polym.* **2011**, *86*, 1723.
12. Cheng, Y.; Brown, K. M.; Prudhomme, R. K. *Int. J. Biol. Macromol.* **2002**, *31*, 29.

13. Seon-Joo, Y.; Djong-Chi, C.; Lekh, R. J. *J. Clin. Biochem. Nutr.* **2008**, *42*, 1.
14. Lapasin, R.; De Lorenzi, L.; Pricl, S.; Torriano, G. *Carbohydr. Polym.* **1995**, *28*, 195.
15. Duxenneuner, M. R.; Fisher, P.; Windhab, E. J.; Cooper-White J. J. *Biomacromolecules* **2008**, *9*, 2989.
16. Zhang, L. M.; Kong, T.; Peter, S. H. *J. Sci. Food Agric.* **2007**, *87*, 684.
17. Hongbo, T.; Min, S.; Yanping, L. *J. Adv. Mater. Res.* **2012**, *518-523*, 3921.
18. Johnson, P. P. *Anal. Chem.* **1969**, *41*, 859.
19. Choi, Y. J.; Lim, S. T.; Im, S. S. *Food Biotechnol.* **1997**, *6*, 118.
20. Wang, Q.; Ellis, P. R.; Ross-Murphy, S. B. *Food Hydrocolloids* **2000**, *14*, 129.
21. Hongbo, T.; Yanping, L.; Min, S.; Xiguang, W. *Polym. J.* **2012**, *44*, 211.
22. Flurer, C. L.; Crowe, J. B.; Wolnik, K. A. *Food Addit. Contam.* **2000**, *17*, 3.
23. Vandana, S.; Ashutosh, T.; Devendra, N. T.; Rashmi, S. *J. Appl. Polym. Sci.* **2004**, *92*, 1569.
24. Naoi, S.; Hatakeyama, T.; Hatakeyama, H. *J. Therm. Anal. Calorim.* **2002**, *70*, 841.